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DOCUMENT-IDENTIFIER: US 6846868 B2
TITLE: Polyamide composition

DATE-ISSUED: January 25, 2005

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
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ASSIGNEE INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY	TYPE CODE
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APPL-NO: 10/161686

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FOREIGN-APPL-PRIORITY-DATA:

COUNTRY	APPL-NO	APPL-DATE
JP	2001-169159	June 5, 2001

INT-CL-ISSUED: [07] C08K003/10 , C08K003/34 , C08G073/10

INT-CL-CURRENT:

TYPE	IPC DATE
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CIPS	<u>C08 G 69/00</u> 20060101
CIPS	<u>C08 G 69/26</u> 20060101
CIPS	<u>C08 K 3/16</u> 20060101
CIPS	<u>C08 K 3/00</u> 20060101

US-CL-ISSUED: 524/413 , 524/443 , 528/322 , 528/335 , 528/340 ,
528/347 , 528/348

US-CL-CURRENT: 524/413 , 524/443 , 528/322 , 528/335 , 528/340 ,
528/347 , 528/348

FIELD-OF-CLASSIFICATION-SEARCH: 524/413; 524/443 ; 528/322 ; 528/335 ; 528/340 ;
528/347 ; 528/348

****See application file for complete search history****

REF-CITED:

U.S. PATENT DOCUMENTS

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>3457325</u>	July 1969	Anton et al.	N/A N/A N/A
<u>3639335</u>	February 1972	Fujii et al.	N/A N/A N/A
<u>4172194</u>	October 1979	Scoggins et al.	N/A N/A N/A
<u>4937276</u>	June 1990	Nielinger et al.	N/A N/A N/A
<u>4963646</u>	October 1990	Galland et al.	N/A N/A N/A
<u>5003009</u>	March 1991	Matthies et al.	N/A N/A N/A
<u>5081222</u>	January 1992	Reimann et al.	N/A N/A N/A
<u>5109106</u>	April 1992	Lahary et al.	N/A N/A N/A
<u>5322923</u>	June 1994	Lahary et al.	N/A N/A N/A
<u>5670608</u>	September 1997	Oka et al.	N/A N/A N/A
<u>5763561</u>	June 1998	Keske	N/A N/A N/A
<u>6156869</u>	December 2000	Tamura et al.	N/A N/A N/A
<u>6258927</u>	July 2001	Oka et al.	N/A N/A N/A
<u>6414064</u>	July 2002	Matsuoka et al.	N/A N/A N/A
<u>6552123</u>	April 2003	Takayashi et al.	525/57 N/A N/A

FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
0 285 692	October 1988	EP	
0 327 979	August 1989	EP	
0 659 799	June 1995	EP	
5-117525	May 1993	JP	
5-140386	June 1993	JP	
7-126516	May 1995	JP	
7-228768	August 1995	JP	
7-228773	August 1995	JP	
9-316731	December 1997	JP	
2001-11308	January 2001	JP	
WO 92/10525	June 1992	WO	
WO 00/78869	December 2000	WO	

ART-UNIT: 1714

PRIMARY-EXAMINER: Sanders; Kriellion A.

ATTY-AGENT-FIRM: Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

ABSTRACT:

A polyamide composition comprising 100 parts by weight of (A) a semiaromatic polyamide having dicarboxylic acid units mainly composed of aromatic dicarboxylic acid units and diamine units mainly composed of aliphatic diamine units having 4 to 14 carbon atoms and containing not more than 15 .mu.eq/g of terminal amino groups; and 0.01 to 5 parts by weight of (B) a copper compound.

20 Claims, 0 Drawing figures

Exemplary Claim Number: 1

Brief Summary Text - BSTX (7):

Another approach to the problem is the preparation of polyamide compositions which comprise a semi-aromatic polyamide. The heat resistance of these polyamide compositions is generally better than that of an aliphatic polyamide, and the incorporation of a copper compound as a stabilizer into the compositions has also been proposed. U.S. Pat. No. 5,003,009 discloses impact resistant nylon molding materials containing (A) a linear, thermoplastic nylon composed of radicals derived from terephthalic acid, isophthalic acid and alkanediamines of 4 to 10 carbon atoms, and (B) one or more copolymers of (i) ethylene, an ester of (meth)acrylic acid and a monomer having an acidic functional group or a latent acidic functional group, or (ii) an ester of (meth)acrylic acid, a monomer having an acidic functional group or a latent acidic functional group and a monomer having 2 or more olefinic double bonds, and, if required, (c) effective amount of additives such as antioxidants and stabilizers, e.g. copper (I) halides. Japanese Patent Application Laid-open No. Hei 7-228768, (JPA 228768/95) discloses a polyamide composition comprising (a) a semiaromatic polyamide having (i) terephthalic acid units and 1,9-**nonanediamine** units or (ii) terephthalic acid units, 1,9-**nonanediamine** units and 2-methyl-1,8-octanediamine units, and having an intrinsic viscosity [.eta.] measured in concentrated sulfuric acid at 30.degree. C. of 0.4 to 3.0 dl/g, (b) a copper compound, (c) an alkali metal halide and (d) an organic stabilizer. Japanese Patent Application Laid-open No. Hei 7-228773 (JPA 228773/95) discloses a polyamide composition comprising (a) a semiaromatic polyamide having (i) terephthalic acid units and 1,9-**nonanediamine** units or (ii) terephthalic acid units, 1,9-**nonanediamine** units and 2-methyl-1,8-octanediamine units, and having an intrinsic viscosity [.eta.] measured in concentrated sulfuric acid at 30.degree. C. of 0.4 to 3.0 dl/g, (b) a copper compound and (c) a nucleating agent. U.S. Pat. No. 5,763,561 discloses an injection moldable composition comprising (a) a semiaromatic polyamide containing about 0 to about 40 .mu.eq/g of carboxylic acid end groups, said polyamide containing aliphatic diamine units of 4 to 14 carbon atoms and terephthalic acid units; and (b) a copper-containing thermal stabilizer formulation comprising an alkali metal halide and a copper (I) halide in a weight ratio ranging from about 2.5:1 to about 20:1.

Brief Summary Text - BSTX (14):

In addition, a semiaromatic polyamide having (i) terephthalic acid units and 1,9-**nonanediamine** units or (ii) terephthalic acid units, 1,9-**nonanediamine** units and 2-methyl-1,8-octanediamine units is described in many patent specifications other than Japanese Patent Application Laid-open Nos. Hei 7-228768 and Hei 7-228773. For example, Japanese Patent Application Laid-open No. Hei 9-316731 discloses a conjugated fiber obtained by (A) a semiaromatic polyamide composed of terephthalic acid units and alkylenediamine units having 6 to 12 carbon atoms and (B) a thermoplastic polymer which is incompatible with the semiaromatic polyamide.

However, the number of terminal amino groups of the semiaromatic polyamide described in these other patent applications are, to the knowledge of the present inventors, 20 .mu.eq/g or more. For example, the number of terminal amino groups of the semiaromatic polyamide described in the Referential Examples 6 and 7 of Japanese Patent Application Laid-open No. Hei 9-316731 is about 30-40 .mu.eq/g.

Detailed Description Text - DETX (5):

The aliphatic diamine units having 4 to 14 carbon atoms include, for example, units derived from linear aliphatic alkylenediamines such as 1,4-tetramethylenediamine, 1,6-hexanediamine, 1,7-heptanediamine, 1,8-octanediamine, 1,9 -nonanediamine, 1,10-decanediamine, 1,11-undecanediamine and 1,12-dodecanediamine; branched aliphatic alkylenediamines such as 2-methyl-1,5-pentanediamine, 3-methyl-1,5-pentanediamine, 2,2,4-trimethyl-1,6-hexanediamine, 2,4,4-trimethyl-1,6-hexanediamine, 2,4-dimethyl-1,6-hexanediamine, 2-methyl-1,8-octanediamine and 5-methyl-1,9 -nonanediamine. The semiaromatic polyamides (A) may contain one or more of these aliphatic diamine units. Preferred among them, in view of production costs and various properties of the semiaromatic polyamides (A) are 1,4-tetramethylenediamine units, 1,6-hexanediamine units, 1,9 -nonanediamine units, 1,10-decanediamine units, 1,12-dodecanediamine units, 2-methyl-1,5-pentanediamine units, 3-methyl-1,5-pentanediamine units or 2-methyl-1,8-octanediamine units; and more preferred are 1,9 -nonanediamine units and/or 2-methyl-1,8-octanediamine units.

Detailed Description Text - DETX (41):

When the sample solution contains undissolved solid matter, such solid matter is discharged by filtration using a 0.5 .mu.m aperture -membrane filter and the filtrate obtained is tested for its inherent viscosity.

Detailed Description Text - DETX (61):

An autoclave having an inner volume of 20 liters was charged with 4634.2 g (27.8 moles) of terephthalic acid, 4432.1 g (28.0 moles) of a mixture of 80% of 1,9 -nonanediamine and 20% of 2-methyl-1,8-octanediamine, 85.5 g (0.70 mole) of benzoic acid, 9.12 g (0.1% by weight based on the total weight of raw materials) of sodium hypophosphite monohydrate and 2.5 liters of distilled water under nitrogen. The resulting mixture was agitated at 100.degree. C. for 30 minutes, then the temperature of the mixture was elevated to 220.degree. C. over 2 hours under agitation. At this time, the inner pressure of the autoclave was 2 MPa. The reaction mixture was agitated at 220.degree. C. for 2 hours, then the temperature of the mixture was elevated to 230.degree. C. with agitation. The reaction was further conducted for 2 hours under constant temperature of 230.degree. C. and pressure of 2 MPa which was kept constant by discharging the water which formed. Thereafter, the inner pressure of the autoclave

was reduced to 1 MPa over 30 minutes and the reaction mixture was further agitated for 1 hour at 230.degree. C. under the pressure of 1 MPa to give a prepolymer having an intrinsic viscosity [η] of 0.18 dl/g. The prepolymer was dried at 100.degree. C. under reduced pressure for 12 hours and then pulverized to a particle size of not more than 2 mm. The particles were subjected to solid phase polymerization at 230.degree. C. under 13 Pa [0.1 mmHg] of pressure for 10 hours to give a white polyamide having a melting point of 306.degree. C., an intrinsic viscosity [η] of 1.51 dl/g, a number of terminal amino groups of 12 .mu.eq/g and a number of terminal carboxyl groups of 42 .mu.eq/g.

Detailed Description Text - DETX (67):

An autoclave having an inner volume of 20 liters was charged with 4601.0 g (27.7 moles) of terephthalic acid, 4432.1 g (28.0 moles) of 1,9-nonanediamine, 116.0 g (0.95 mole) of benzoic acid, 9.12 g (0.11% by weight based on the total weight of raw materials) of sodium hypophosphite monohydrate and 2.5 liters of distilled water under nitrogen. The resulting mixture was agitated at 100.degree. C. for 30 minutes, and then the temperature of the mixture was elevated to 220.degree. C. over 2 hours under agitation. At this time, the inner pressure of the autoclave was 2 MPa. The reaction mixture was agitated at 220.degree. C. for 2 hours, and then the temperature of the mixture was elevated to 230.degree. C. under agitation. The reaction was further conducted for 2 hours under constant temperature of 230.degree. C. and a pressure of 2 Ma which was kept constant by discharging the water which formed. Thereafter, the inner pressure of the autoclave was reduced to 1 MPa over 30 minutes and the reaction mixture was further agitated for 1 hour at 230.degree. C. under a pressure of 1 MPa to give a prepolymer having an intrinsic viscosity [η] of 0.15 dl/g. The prepolymer was dried at 100.degree. C. under reduced pressure for 12 hours and then pulverized to a particle size of not more than 2 mm. The particles were subjected to solid phase polymerization at 230.degree. C. under 13 Pa [0.1 mmHg] of pressure for 10 hours to give a white polyamide having a melting point of 317.degree. C., an intrinsic viscosity [η] of 1.30 dl/g, a number of terminal amino groups of 9 .mu.eq/g and a number of terminal carboxyl groups of 41 .mu.eq/g. This polyamide was abbreviated as "PA9T-2".

Detailed Description Text - DETX (72):

An autoclave having an inner volume of 20 liters was charged with 4667.4 g (28.1 moles) of terephthalic acid, 4432.1 g (28.0 moles) of a mixture of 80% of 1,9-nonanediamine and 20% of 2-methyl-1,8-octanediamine, 102.6 g (0.84 mole) of benzoic acid, 9.20 g (0.1% by weight based on the total weight of raw materials) of sodium hypophosphite monohydrate and 2.5 liters of distilled water under nitrogen. The resulting mixture was agitated at 100.degree. C. for 30 minutes, then the temperature of the mixture was elevated to 220.degree. C. over 2 hours under agitation. At this time, the inner pressure of the autoclave was 2 MPa. The reaction mixture was agitated at

220.degree. C. for 2 hours, and then the temperature of the mixture was elevated to 230.degree. C. under agitation. The reaction was further conducted for 2 hours under constant temperature of 230.degree. C. and a pressure of 2 MPa which was kept constant by discharging the water which formed. Thereafter, the inner pressure of the autoclave was reduced to 1 MPa over 30 minutes and the reaction mixture was further agitated for 1 hour at 230.degree. C. under the pressure of 1 MPa to give a prepolymer having an intrinsic viscosity [η] of 0.16 dl/g. The prepolymer was dried at 100.degree. C. under reduced pressure for 12 hours and then pulverized to a particle size of not more than 2 mm. The particles were subjected to solid phase polymerization at 230.degree. C. under 13 Pa [0.1 mmHg] of pressure for 10 hours to give a white polyamide having a melting point of 306.degree. C., an intrinsic viscosity [η] of 0.90 dl/g, a number of terminal amino groups of 12 $\mu\text{eq/g}$ and a number of terminal carboxyl groups of 76 $\mu\text{eq/g}$. This polyamide was abbreviated as "PA9T-3".

Detailed Description Text - DETX (78):

An autoclave having an inner volume of 20 liters was charged with 4584.4 g (27.6 moles) of terephthalic acid, 4527.1 g (28.6 moles) of a mixture of 80% of 1,9-nonanediamine and 20% of 2-methyl-1,8-octanediamine, 102.6 g (0.84 mole) of benzoic acid, 9.21 g (0.1% by weight based on the total weight of raw materials) of sodium hypophosphite monohydrate and 2.5 liters of distilled water under nitrogen. The resulting mixture was agitated at 100.degree. C. for 30 minutes, then the temperature of the mixture was elevated to 220.degree. C. over 2 hours under agitation. At this time, the inner pressure of the autoclave was 2 MPa. The reaction mixture was agitated at 220.degree. C., for 2 hours, and then the temperature of the mixture was elevated to 230.degree. C. with agitation. The reaction was further conducted for 2 hours at constant temperature of 230.degree. C. and pressure of 2 MPa which was kept constant by discharging the water which had formed. Thereafter, the inner pressure of the autoclave was reduced to 1 MPa over 30 minutes and the reaction mixture was further agitated for 1 hour at 230.degree. C. under the pressure of 1 MPa to give a prepolymer having an intrinsic viscosity [η] of 0.16 dl/g. The prepolymer was dried at 100.degree. C. under reduced pressure for 12 hours and then pulverized to a particle size of not more than 2 mm. The particles were subjected to solid phase polymerization at 230.degree. C. under 13 Pa [0.1 mmHg] of pressure for 10 hours to give a white polyamide having a melting point of 306.degree. C., an intrinsic viscosity [η] of 1.40 dl/g, a number of terminal amino groups of 30 $\mu\text{eq/g}$ and a number of terminal carboxyl groups of 16 $\mu\text{eq/g}$. This polyamide was abbreviated as "PA9T-4".

Detailed Description Text - DETX (88):

An autoclave having an inner volume of 20 liters was charged with 3322 g (20.0 moles) of terephthalic acid, 3166 g (20.0 moles) of 1,9-nonanediamine, 48.8 g (0.4

mole) of benzoic acid, 5.28 g (0.06 mole) of sodium hypophosphite monohydrate and 2.2 liters of distilled water under nitrogen. The resulting mixture was agitated at 100.degree. C. for 30 minutes, then the temperature of the mixture was elevated to 210.degree. C. over 2 hours with agitation. At this time, the inner pressure of the autoclave was 2.2 MPa. The reaction mixture was agitated at 210.degree. C., for 1 hours, and then the temperature of the mixture was elevated to 230.degree. C. under agitation. The reaction was further conducted for 2 hours under constant temperature of 230.degree. C. and pressure of 2.2 MPa which was kept constant by discharging the water which formed. Thereafter, the inner pressure of the autoclave was reduced to 1 MPa over 30 minutes and the reaction mixture was further agitated for 1 hour at 230.degree. C. under the pressure of 1 MPa to give a prepolymer having an intrinsic viscosity [.eta.] of 0.17 dl/g. The prepolymer was dried at 100.degree. C. under reduce pressure for 12 hours and then pulverized to a particle size of not more than 2 mm. The particles were subjected to solid phase polymerization at 230.degree. C., under 13Pa [0.1 mmHg] of pressure for 10 hours to give a white polyamide having a melting point of 312.degree. C., an intrinsic viscosity [.eta.] of 1.11 dl/g, a number of terminal amino groups of 32 .mu.eq/g and a number of terminal carboxyl groups of 10 .mu.eq/g. This polyamide was abbreviated as "PA9T-5".

Detailed Description Text - DETX (94):

An autoclave having an inner volume of 20 liters was charged with 3355 g (20.2 moles) of terephthalic acid, 2691 g (17.0 moles) of 1,9 -nonanediamine, 475 g (3.0 moles) of 2-methyl-1,8-octanediamine, 36.6 g (0.3 mole) of benzoic acid, 5.28 g (0.06 mole) of sodium hypophosphite monohydrate and 2.2 liters of distilled water under nitrogen. The resulting mixture was agitated at 100.degree. C. for 30 minutes, then the temperature of the mixture was elevated to 210.degree. C., over 2 hours with agitation. At this time, the inner pressure of the autoclave was 2.2 MPa. The reaction mixture was agitated at 210.degree. C. for 1 hour, then the temperature of the mixture was elevated to 230.degree. C. with agitation. The reaction was further conducted for 2 hours under constant temperature of 230.degree. C. and pressure of 2.2 MPa which was kept constant by discharging the water which had formed. After that, the inner pressure of the autoclave was reduced to 1 MPa over 30 minutes and the reaction mixture was further agitated for 1 hour at 230.degree. C. under the pressure of 1 MPa to give a prepolymer having an intrinsic viscosity [.eta.] of 0.20 dl/g. The prepolymer was dried at 100.degree. C. under reduced pressure for 12 hours and then pulverized to a particle size of not more than 2 mm. The particles were subjected to solid phase polymerization at 230.degree. C., under 13 Pa [0.1 mmHg] of pressure for 10 hours to give a white polyamide having a melting point of 299.degree. C., an intrinsic viscosity [.eta.] of 1.02 dl/g, a number of terminal amino groups of 44 .mu.eq/g and a number of terminal carboxyl groups of 9 .mu.eq/g. This polyamide was abbreviated as "PA9T-6".

Detailed Description Text - DETX (100):

An autoclave having an inner volume of 20 liters was charged with 3272.9 g (19.7 moles) of terephthalic acid, 2849.2 g (18.0 moles) of 1,9-**nonanediamine**, 316.58 g (2.0 moles) of 2-methyl-1,8-octanediamine, 73.27 g (0.6 mole) of benzoic acid, 6.5 g of sodium hypophosphite monohydrate and 2.2 liters of distilled water under nitrogen. The resulting mixture was agitated at 100.degree. C. for 30 minutes, and then the temperature of the mixture was elevated to 210.degree. C. over 2 hours under agitation. At this time, the inner pressure of the autoclave was 2.2 MPa. The reaction mixture was agitated at 210.degree. C. for 1 hours, and then the temperature of the mixture was elevated to 230.degree. C. under agitation. The reaction was further conducted for 2 hours under constant temperature of 230.degree. C. and pressure of 2.2 MPa which was kept constant by discharging the water which had formed. After that, the inner pressure of the autoclave was reduced to 1 MPa over 30 minutes and the reaction mixture was further agitated for 1 hour at 230.degree. C. under the pressure of 1 MPa to give a prepolymer having an intrinsic viscosity [η] of 0.20 dl/g. The prepolymer was dried at 100.degree. C. under reduced pressure for 12 hours and then pulverized to a particle size of not more than 2 mm. The particles were subjected to solid phase polymerization at 230.degree. C. under 13 Pa [0.1 mmHg] of pressure for 10 hours to give a white polyamide having a melting point of 305.degree. C., an intrinsic viscosity [η] of 1.23 dl/g, a number of terminal amino groups of 23 . μ eq/g and a number of terminal carboxyl groups of 28 . μ eq/g. This polyamide was abbreviated as "PA9T-7".

Claims Text - CLTX (2):

2. The polyamide composition of claim 1, wherein 60 to 100 mole % of said dicarboxylic acid unit is terephthalic acid unit and 60 to 100 mole % of said diamine unit is 1,9-**nonanediamine** unit and/or 2-methyl-1,8-octanediamine unit.

Claims Text - CLTX (3):

3. The polyamide composition of claim 2, wherein 70 to 100 mole % of said dicarboxylic acid unit is terephthalic acid unit and 70 to 100 mole % of said diamine unit is 1,9-**nonanediamine** unit and/or 2-methyl-1,8-octanediamine unit.

Claims Text - CLTX (12):

12. The polyamide composition of claim 1, wherein the aliphatic diamine of the aliphatic diamine units having 4 to 14 carbon atoms is a linear aliphatic alkylenediamine selected from the group consisting of 1,4-tetramethylenediamine, 1,6-hexanediamine, 1,7-heptanediamine, 1,8-octanediamine, 1,9-**nonanediamine**, 1,10-decanediamine, 1,11-undecanediamine and 1,12-dodecanediamine or a branched aliphatic alkylenediamine selected from the group consisting of 2-methyl-1,5-pentanediamine, 3-methyl-1,5 pentanediamine, 2,2,4-trimethyl-1,6-hexanediamine, 2,4,4-trimethyl-1,6-

hexanediamine, 2,4-dimethyl-1,6-hexanediamine, 2-methyl-1,8-octanediamine, 5-methyl-1,9 **-nonanediamine**, and combinations thereof.

EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	446	(210/500.38).CCLS.	USPAT; EPO; DERWENT	OR	OFF	2007/09/03 16:32
L2	0	210/500.38./ccls.	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:33
L3	446	210/500.38.ccls.	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:33
L4	320	3 and polyamide and membrane	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:34
L5	9	4 and "water absorption"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:34
L6	0	4 and "water absorption" same "10 %"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:34
L7	1	5 and "dicarboxylic acid"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:42
L8	0	7 and nonanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:35
L9	0	3 and "dicarboxylic acid" and "nonanediamine"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:43
L10	0	3 and "dicarboxylic acid" and "nonanediamine"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:43
L11	0	3 and "dicarboxylic acid" and nonanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:44
L12	92	3 and "dicarboxylic acid"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:44
L13	32	12 and "terephthalic acid"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:45
L14	0	13 and octanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:45
L15	0	13 and nonanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:46

EAST Search History

L16	0	13 and nonane-diamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:46
L17	199	nonanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:46
L18	18	17 and membrane	USPAT; EPO; DERWENT	AND	ON	2007/09/03 17:27
L19	0	18 and 3	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:46
L20	1	"pa9t-7"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 17:28

EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	446	(210/500.38).CCLS.	USPAT; EPO; DERWENT	OR	OFF	2007/09/03 16:32
L2	0	210/500.38./ccls.	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:33
L3	446	210/500.38.ccls.	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:33
L4	320	3 and polyamide and membrane	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:34
L5	9	4 and "water absorption"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:34
L6	0	4 and "water absorption" same "10 %"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:34
L7	1	5 and "dicarboxylic acid"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:42
L8	0	7 and nonanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:35
L9	0	3 and "dicarboxylic acid" and "nonanediamine"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:43
L10	0	3 and "dicarboxylic acid" and "nonanediamine"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:43
L11	0	3 and "dicarboxylic acid" and nonanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:44
L12	92	3 and "dicarboxylic acid"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:44
L13	32	12 and "terephthalic acid"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:45
L14	0	13 and octanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:45
L15	0	13 and nonanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:46

EAST Search History

L16	0	13 and nonane-diamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:46
L17	199	nonanediamine	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:46
L18	18	17 and membrane	USPAT; EPO; DERWENT	AND	ON	2007/09/03 17:27
L19	0	18 and 3	USPAT; EPO; DERWENT	AND	ON	2007/09/03 16:46
L20	1	"pa9t-7"	USPAT; EPO; DERWENT	AND	ON	2007/09/03 17:28

US-PAT-NO: 4935141
DOCUMENT-IDENTIFIER: US 4935141 A

****See image for Certificate of Correction****

TITLE: Selectively permeable **asymmetric membranes** suitable for use in hemodialysis and processes for manufacturing such **membranes**

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INVENTOR-INFORMATION:

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REF-CITED:**U.S. PATENT DOCUMENTS**

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL
<u>4051300</u>	September 1977	Klein	264/184 N/A N/A
<u>4286015</u>	August 1981	Yoshida et al.	N/A 264/177.14 N/A
<u>4664669</u>	May 1987	Ohyabu et al.	427/245 N/A N/A
<u>4720343</u>	January 1988	Walch et al.	210/500.28 N/A N/A

FOREIGN PATENT DOCUMENTS

FOREIGN-PAT-NO	PUBN-DATE	COUNTRY	US-CL
EP0168783	July 1985	EP	
60-246812	December 1985	JP	
61-257203	November 1986	JP	
WO8600028	January 1986	WO	

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ABSTRACT:

Selectively permeable asymmetric membranes are disclosed which are suitable for use in hemodialysis processes and the like. The membranes are produced from hydrophobic and hydrophilic polymers, and include a three-layered structure including a first dense thin skin layer which includes uniform pores of a size whereby proteins having a molecular weight of at least that of albumin are substantially rejected therefrom, an intermediate second layer in the form of a sponge and having a higher diffusive permeability than the first layer, and a third layer with a finger-like structure which provides mechanical stability. These membranes are preferably formed in the shape of hollow fibers, with the first layer as the inner layer thereof. Processes for manufacturing these membranes are also disclosed, and include separately mixing both the hydrophobic and hydrophilic polymers in solvents therefor, and then mixing these two solutions before extruding the mixture into a precipitating liquid to form the precipitated membrane by a wet-phase inversion technique.

42 Claims, 8 Drawing figures

Exemplary Claim Number: 1

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Abstract Text - ABTX (1):

Selectively permeable asymmetric membranes are disclosed which are suitable for use in hemodialysis processes and the like. The membranes are produced from hydrophobic and hydrophilic polymers, and include a three-layered structure including a first dense thin skin layer which includes uniform pores of a size whereby proteins having a molecular weight of at least that of albumin are substantially rejected therefrom, an intermediate second layer in the form of a sponge and having a higher diffusive permeability than the first layer, and a third layer with a finger-like structure which provides mechanical stability. These membranes are preferably formed in the shape of hollow fibers, with the first layer as the inner layer thereof. Processes for manufacturing these membranes are also disclosed, and include separately mixing both the hydrophobic and hydrophilic polymers in solvents therefor, and then mixing these two

solutions before extruding the mixture into a precipitating liquid to form the precipitated **membrane** by a wet-phase inversion technique.

TITLE - TI (1):

Selectively permeable **asymmetric membranes** suitable for use in hemodialysis and processes for manufacturing such **membranes**

Brief Summary Text - BSTX (2):

The present invention relates to selectively permeable **asymmetric membranes**. More particularly, the present invention relates to such **membranes** suitable for use in processes such as hemodialysis. Still more particularly, the present invention relates to such **asymmetric membranes** which include a hydrophobic first polymer, a hydrophilic second polymer, and suitable additives. Still more particularly, the present invention relates to processes for manufacturing such selectively permeable **asymmetric membranes**.

Brief Summary Text - BSTX (4):

Selectively permeable (also referred to as permselective) **asymmetric membranes** are particularly advantageous when used in connection with various types of medical treatments, such as hemodialysis, hemofiltration, plasmapheresis, and immunotherapy. Such **membranes** may also be used in connection with dialysis and filtration in general, such as in connection with cleaning or depyrogenization of **water**.

Brief Summary Text - BSTX (5):

These types of **membranes** are described in detail, for example, in EP-A-O168 783, EP-B-O082 433, and WO 86/00028. The contents of these publications are therefore included in the present application by reference thereto. Referring specifically to the latter publication (WO 86/00028), there is disclosed therein asymmetrical hollow fiber **membranes** which include a relatively dense skin layer of less than about 1 micron on their outer periphery, bounded by an open structure of increasing porosity towards the inner surface of the hollow fibers, which **porous** structure comprises micro-voids having the shape of elongated fingers open to the inner surface of the **membranes**. This publication also discloses the methods of obtaining these **asymmetric** hollow fibers via known spinning techniques by a dry-wet process which includes adding to the spinning solution of the polymer in the solvent at least one specified additive and adding a particular fluid through the center. FIG. 7 in this publication shows this particular structure.

Brief Summary Text - BSTX (6):

The other two cited publications also disclose asymmetric membranes of this type comprised of mixtures of hydrophobic and hydrophilic polymers.

Brief Summary Text - BSTX (8):

In accordance with the present invention, membranes of the above-described type, namely selectively permeable asymmetric membranes which are suitable for use in hemodialysis, have been produced by providing a novel integral three-layered structure which includes a first layer in the form of a dense, rather thin skin, which is responsible for the sieving properties of the membrane, a second layer in the form of a sponge structure, having high diffusive permeability and which serves as a support for the first layer, and a third layer in the form of an open finger-like structure which provides the membrane with structural stability. The advantages obtained by using such a structure are explained in more detail herein.

Brief Summary Text - BSTX (9):

Most particularly, in accordance with the present invention, the applicants have provided a selectively permeable asymmetric membrane comprising a hydrophobic polymer and a hydrophilic polymer in which the membrane includes a first layer comprising a dense, thin skin layer including substantially uniform pore openings defining the selective permeability of the membrane, an intermediate second layer in contact with the first layer in the form of a sponge having a diffusive permeability which is higher than that of the first layer, the intermediate second layer supporting the first layer, and a third layer in contact with the intermediate second layer and including a finger-like structure providing mechanical stability for the membrane, the substantially uniform pore openings in the first layer having a size whereby proteins which have a molecular weight of at least that of albumin are substantially completely rejected from the membrane. In a preferred embodiment, the pore openings have a pore size not greater than about 80 Angstroms.

Brief Summary Text - BSTX (10):

In accordance with another embodiment of the membranes of the present invention, they may be in the form of a substantially flat sheet or in the form of hollow fibers, in which case the first layer preferably comprises the inner layer of the hollow fiber, and the third layer preferably comprises the outer layer of the hollow fiber.

Brief Summary Text - BSTX (11):

In accordance with another embodiment of the membranes of the present invention, they are prepared from a polymer mixture including the hydrophobic and hydrophilic polymers in amounts such that the fraction of hydrophobic polymer is between about 85

and 95% thereof and the fraction of hydrophilic polymer is between about 5 and 15% thereof.

Brief Summary Text - BSTX (12):

In accordance with a preferred embodiment of the membranes of the present invention the hydrophobic polymer can be a polyarylsulfone, polycarbonate, polyamide, polyvinylchloride, modified acrylic acid, polyether, polyurethane, polyetherketone, polyacrylonitrile, polypropylene, polyetherimide and copolymers thereof, and most preferably a polyamide. In addition, the hydrophilic polymers preferably are polyvinylpyrrolidone, polyethyleneglycol, polyglycolmonoester, copolymers of polyethyleneglycol with polypropyleneglycol, water soluble cellulosic derivatives, polysorbate, and polyethylene-polypropylene oxide copolymers, and most preferably polyvinylpyrrolidone.

Brief Summary Text - BSTX (13):

In accordance with another embodiment of the present invention, processes for manufacturing selectively permeable asymmetric membranes suitable for use in hemodialysis have now been discovered, and include dissolving a hydrophobic polymer in a first solvent so as to prepare a first solution, dissolving a hydrophilic polymer in a second solvent so as to prepare a second solution, mixing the first and second solutions, and introducing that mixture into a precipitating liquid to form a coagulated membrane therefrom. In a preferred embodiment, mixing of the first and second solutions is conducted at a first temperature, preferably about 60.degree. C., and introduction of the mixture into the precipitating liquid is conducted at a second temperature, which is preferably lower than the first temperature, and is preferably below about 30.degree. C.

Brief Summary Text - BSTX (14):

In accordance with a preferred embodiment of the process of the present invention, the first and second solvents can be dimethylacetamide, dimethylformamide, dimethylsulfoxide, n-methylpyrrolidone, and preferably dimethylsulfoxide. Preferably, the precipitating liquid also includes a solvent for the hydrophilic polymer, such as water, as well as a solvent for the hydrophobic polymer, such as dimethylsulfoxide. Most preferably, the precipitating liquid also includes a hydrophilic polymer, such as the polyvinylpyrrolidone.

Drawing Description Text - DRTX (3):

FIG. 1a is a scanning electromicroscopic photograph of the membrane structure in accordance with the present invention;

Drawing Description Text - DRTX (4):

FIG. 1b is another scanning electromicroscopic photograph of the membrane structure in accordance with the present invention;

Drawing Description Text - DRTX (5):

FIG. 2a is a more detailed transmission electromicroscopic photograph of the skin and porous layer structure of the membrane of the present invention;

Drawing Description Text - DRTX (6):

FIG. 2b is another more detailed transmission electromicroscopic photograph of the skin and porous layer structure of the membrane of the present invention;

Drawing Description Text - DRTX (7):

FIG. 3 is a graph of the sieving coefficients of membranes which include membranes in accordance with the present invention.

Drawing Description Text - DRTX (8):

FIG. 4 is a compilation of the results of protein absorption measurements on the membranes shown in FIG. 3;

Drawing Description Text - DRTX (9):

FIG. 5 is a graph of the increase of complement factors C.sub.3a during the initial phase of dialysis treatment for various membranes;

Drawing Description Text - DRTX (10):

FIG. 6 is a graph of the number of leucocytes in a patient's blood by hemodialysis using a membrane in accordance with the present invention;

Drawing Description Text - DRTX (11):

FIG. 7 is a graph of the ultrafiltration rate of the membrane in accordance with the present invention at various transmembrane pressures and blood flows; and

Drawing Description Text - DRTX (12):

FIG. 8 is a graph of the urea clearance for membranes according to the present invention at various blood flows.

Detailed Description Text - DETX (2):

The selectively permeable asymmetric membranes in accordance with the present invention have an asymmetric structure which is characterized by three integral layers, each of which has a different structure and function. These three integral layers thus include:

Detailed Description Text - DETX (3):

(a) a smooth and dense homogeneous thin (preferably <1.mu.) layer, which determines the sieving properties of the membrane;

Detailed Description Text - DETX (4):

(b) a porous (sponge-like) layer (preferably having a thickness of about 1-20.mu., and most preferably of about 3-5.mu.) which determines the mechanical stability of the inner layer (layer (a)), and which acts as a safety barrier should inner layer (a) have a defect; and

Detailed Description Text - DETX (5):

(c) an open finger-like supporting layer, which provides the membrane with its mechanical stability for trans -membrane pressures and stresses which arise during manufacturing and/or handling thereof.

Detailed Description Text - DETX (6):

This membrane structure demonstrates outstanding properties for the various blood purification techniques, such as hemodialysis, hemodiafiltration and hemofiltration, particularly because it has a high diffusive permeability for low molecular weight substances, a high permeability for middle molecular weight substances (i.e., with molecular weights between about 1,000 and 15,000), such as .beta..sub.2 -microglobulin (M.sub.w 11,500), and it has an ultrafiltration rate which is readily adaptable to hemodialysis, hemodiafiltration and hemofiltration, as well as outstanding biocompatibility.

Detailed Description Text - DETX (7):

When the membrane of this invention is manufactured in the form of a hollow fiber, the inner layer or blood side includes the skin layer, with a thickness of preferably less than about 1.mu.. The substantially uniform pores in this skin layer are typically in the range of between about 20 and 200 Angstroms, preferably between about 20 and 80 Angstroms, i.e., most preferably of about 80 Angstroms, and this layer determines the

sieving and permeability properties of the membrane. The second intermediate layer is then the sponge-like structure, preferably with a thickness of about 5.mu.. This layer mechanically supports the primary skin layer, and provides the skin with continuous reinforcement as well as an improved resistance to burst and leakages (pin holes). The third layer has an open finger-like structure, with a thickness of about 20 to 60.mu., and preferably about 40.mu.. The void volume in this layer is high, and provides low resistance for convective (filtration) and diffusive transport.

Detailed Description Text - DETX (8):

The scanning electromicroscopic (SEM) pictures set forth in FIGS. 1a and 1b show the entire three-layered membrane structure. Those in FIGS. 2a and 2b shown in more detail the inner skin and porous intermediate layers. In order to obtain these pictures the membranes had to be prepared in the following manner: the frozen membrane was first cut into microtom slides; the membrane slides were then etched and coated with carbon or platinum; and the replica was then magnified with TEM.

Detailed Description Text - DETX (9):

In the above-mentioned publication EP-A-O 168 783, a membrane is described for use in similar applications as is the case with the membrane according to the present invention, but in that case it includes the sponge-like structure throughout its entire thickness. The inner side of the membrane according to that publication demonstrates a pore size of about 150 Angstrom under the microscope. The pores thereof then increase from the inner to the outer side. The disadvantage of such a membrane is that proteins can penetrate into the structure of the membrane, and thus alter the membrane's permeability.

Detailed Description Text - DETX (10):

The membranes of the present invention have a high diffusive permeability for substances which are to be removed in hemodialysis. Urea is one of these substances which is generally used as a characterizing test substance therefor. The diffusive permeability (Pm) measured (according to the method described in NIH Report 77-1294 entitled "Evaluation of Hemodialyzers and Dialysis Membranes") in a test cell is much higher than corresponding values measured for a membrane in accordance with the above-mentioned publication EP-B-O 082 433. (The membrane of this publication is used for comparative purposes herein particularly since the membranes of the present invention were primarily intended to be an improvement over membranes such as those of EP-B-O 082 433). The Pm values of membranes according to the present invention are between about 110 and 150.times.10.sup.-5 cm/sec, whereas this publication reports Pm values of about 75.times.10.sup.-5 cm/sec (45.times.10.sup.-3 cm/min).

Detailed Description Text - DETX (11):

The diffusive permeability of a membrane determines the clearance of a hemodialyzer. The mathematical description of this relationship is: ##EQU1## The high P_m values of the membranes according to the present invention thus correspond to clearance values for a 1 m.sup.2 -dialyzer of between about 175 and 185 ml/min at the standard conditions of 200 ml/min. blood flow and 500 ml/min dialysate flow and TMP (trans -membrane pressures) of 0 mmHg measured with whole blood. The high diffusive permeability of these membranes is a result of the low diffusive resistance of the membrane, which is caused by the high degree of hydrophilicity of the membrane and the above-described open structure thereof.

Detailed Description Text - DETX (12):

Hemodialysis, hemodiafiltration and hemofiltration membranes are also characterized by their ultrafiltration permeability (other expressions are hydraulic or mechanical permeability, or convective permeability). High ultrafiltration rates are desired for hemofiltration and hemodiafiltration processes. The membranes according to the present invention demonstrate much higher ultrafiltration rates for water (about 400 ml/h mmHg.m.sup.2, measured at 37.degree. C.) than most other membranes. The membrane according to EP-A-O 082 433, for example, is reported to show a significantly lower ultrafiltration rate (200.times.10.sup.-3 l /m.sup.2.d.bar, corresponding to 110 ml/h.mmHg.m.sup.2).

Detailed Description Text - DETX (13):

Membranes which are intended for use in hemodialysis and hemofiltration on one hand required the above-described high permeability, while on the other hand they must also reject proteins with high molecular weight. For albumin (M.sub.w 68,000) the rejection should be infinite or close to infinite. Otherwise, the patient will lose essential proteins.

Detailed Description Text - DETX (15):

With the membranes of the present invention, the combination of these two requirements can now be fulfilled, i.e., it is now possible to not only provide a high sieving coefficient (S) of at least about 0.6, e.g., between about 0.6 and 0.8, for .beta..sub.2 -microglobulin, but at the same time provide a low sieving coefficient for albumin, of about 0.001. These sieving properties have been measured in clinical treatment on human blood. In this regard, S can be defined as follows: ##EQU2## Referring specifically to FIG. 3 hereof, it can be noted that these sieving characteristics are achieved because the membranes according to the present invention have a very narrow pore size distribution in the inner membrane skin. In contrast to the membranes

according to EP-A-O 168 783, the inner skin membrane layer according to the present invention (which is responsible for the sieving properties) is very thin. The thinner this thin layer is, the more homogeneous a pore size can be achieved therein.

Detailed Description Text - DETX (16):

Another advantage of the membranes according to the present invention is that the difference between the sieving coefficients, measured in water (in vitro) and in plasma or whole blood (in vivo), respectively, is small. Once again referring to FIG. 3, there is also shown therein for comparative purposes the sieving coefficient of a membrane made from the same hydrophobic PA (polyamide) material, but without the addition of the hydrophilic polymer. In that membrane there is shown to be a significantly large difference between "in vitro" and "in vivo" sieving.

Detailed Description Text - DETX (17):

The reason for the negligible difference therebetween with the membranes of the present invention is the lower protein adsorption for these membranes. This reduced adsorption of proteins decreases the risk that there will be a change in the membrane pore sizes. This adsorption was investigated by a method which is described in Ritz et al, "Protein Layer Formation on Artificial Membranes," (C Tegernsee-symposium, March 1986), Contribution to Nephrology No. 50, Karger, Basel, which is incorporated herein by reference thereto.

Detailed Description Text - DETX (18):

Turning to FIG. 4, this figure presents the results of adsorption measurements on both types of membranes, and clearly shows that much higher amounts of protein can be rinsed back and eluted from the more hydrophobic membranes of the above-mentioned publication.

Detailed Description Text - DETX (19):

These results demonstrate that in the membranes of the present invention less proteins are adsorbed on the membrane and in the membrane pores. The effect of this is that only a small or essentially no change of the effective pore size and the sieving properties of these membranes are shown.

Detailed Description Text - DETX (20):

Referring again to FIG. 4, it can also be noted that TBS stands for trisbuffered solution, and that part III of this Figures shows the qualitative results of the elution of the membrane with three different elution fluids, namely, SDS/Triton solution (sodium

dodecylsulfate), urea solution, and sodium chloride solution. These elution fluids were used subsequent to the rinsing procedures shown in parts I and II, respectively, in order to eluate the residual proteins. The SDS/Triton solution dissolves hydrophobic-hydrophilic binding sites, the urea dissolves the hydrogen binding sites, and the NaCl dissolves the ionic sites. No proteins could be detected in these fluids from the membranes of the present invention (in this case PA/PVP).

Detailed Description Text - DETX (21):

In the case where these membranes are to be used in hemodialysis, the membranes should thus also reject bacteriological materials. It has however, been found in some clinical studies that endotoxins, for example, may pass through the cellulosic membranes which are normally used for dialysis, and thus cause fever reactions.

Detailed Description Text - DETX (22):

With the membranes of the present invention, however, this risk is reduced by its very high rejection capability of bacteriological material. Endotoxins (from E-coli) are thus rejected by these membranes with a logarithmic reduction of about 3.5 to 4.5. The reason for this excellent rejection for endotoxins and other such bacteriological material is that the pore sizes of the inner skin layer hereof are within a very narrow range, and that the maximum pore size does not exceed about 80 Angstrom (=0.008.mu.). The logarithmic reduction value (LRV) can be defined as follows: ##EQU3## where LRV=3 means: 999 out of 1000 endotoxins are eliminated.

Detailed Description Text - DETX (24):

It is also reported, for example, that cellulosic membranes like Cuprophane or saponified cellulose might activate the complement system. This activation can be measured by an increase in the complement factors C.sub.3a, C.sub.3d, C.sub.5a, and primarily C.sub.3a, during the first 15 to 20 minutes of the dialysis treatment. Whereas Cuprophane shows an increase of the C.sub.3a factor concentration in the patient's blood from 10 to 7,000 ng/ml (see FIG. 5), there was no such increase measured for the membranes according to the present invention when it was made according to the above examples.

Detailed Description Text - DETX (25):

Another parameter is the change of leucocyte cells in the blood during the dialysis treatment. Once again, by using Cuprophane membranes, the number of leucocytes in the patient's blood drops within the first 15 to 20 minutes to about 20% of the initial value. Only a small drop to about 90% of the initial value is seen, however, with the membranes made in accordance with the above examples (see FIG. 6).

Detailed Description Text - DETX (27):

The manufacture of the membranes according to the present invention utilizes a phase inversion process, in which a polymer or a mixture of polymers is dissolved in a solvent. The solution is then extruded through a spinning nozzle (for hollow fibers) or a slit nozzle (for flat films) into a fluid bath containing a non-solvent for the polymer. The non-solvent then replaces the solvent, and the polymer is thus precipitated to an inverted solid phase.

Detailed Description Text - DETX (28):

For the membranes of the present invention the hydrophobic polymer, the hydrophilic polymer and an additive are mixed in the following manner: the hydrophobic polymer, preferably polyamide, is first dissolved in a solvent, preferably DMSO (dimethylsulfoxide); and the hydrophilic polymer, preferably PVP (polyvinylpyrrolidone), is then separately premixed in a solvent, preferably DMSO. These two solutions are then mixed together, at an elevated temperature, preferably about 60.degree. C., and also utilizing high shear forces or ultrasonic equipment. The solution must then be cooled, preferably below about 30.degree. C.

Detailed Description Text - DETX (29):

If this process is not followed the PVP will form aggregates. In that case, during the membrane-forming process these PVP aggregates will precipitate and be washed out, leaving microholes in the membrane.

Detailed Description Text - DETX (30):

Before extrusion, any possible additives are then mixed into the mixture of these two solutions (of the hydrophilic and hydrophobic polymers). These additives are used in order to form proper pore structures and to optimize therewith the membrane permeability, the hydraulic and diffusive permeability and the sieving properties. These additives may be said to operate as pore controllers. Substances which may be used for this purpose are non-solvents or relatively weak solvents for the hydrophobic polymer, preferably alcohols, glycerols and water.

Detailed Description Text - DETX (31):

In order to provide a hollow fiber membrane according to the present invention, the above mixture is extruded through a nozzle having two concentric openings. The polymer solution is extruded through the outer ring slit, and the center fluid is extruded through the inner core opening, preferably comprising the non-solvent for the hydrophobic polymer. The fiber is then immersed in baths of non-solvents or fluids

which can replace and wash out the solvent. Polar solvents like DMF, DMSO or DMAc are preferably used as the solvents.

Detailed Description Text - DETX (32):

In order to achieve an optimal structure in the membranes according to this invention (the three integral layers hereof) the center fluid (for a hollow fiber), or the first precipitation fluid bath (for a flat film) should preferably be a mixture of the hydrophilic polymer, an additive and a solvent, i.e., mixed with the non-solvent. It has been found that with this preferred composition (for the center fluid and the above-described polymer solution) the typical integral three-layer structure hereof is formed. Depending on the ratio of the components the three layers have different thicknesses. The present invention may be more fully appreciated with reference to the following examples thereof.

Detailed Description Text - DETX (34):

In accordance with the above-described manufacturing technique, 13 wt. % polyamide was dissolved in a solution containing three wt. % PVP (M.sub.w 100,000), 3 wt. % water, and 81 wt. % DMSO. This polymer solution was degassed and filtered, and then pumped through a concentric hollow fiber spinning jet. The polymer was extruded through an outer ring slit with an outer diameter of about 0.35 mm, and an inner diameter of about 0.25 mm. From the inner orifice of the jet a solution of 30% DMSO, 3% PVP, and 67% water was extruded.

Detailed Description Text - DETX (35):

A hollow fiber was thus formed with a 215.mu. inner diameter and 50.mu. wall thickness. This fiber was then washed thoroughly with non-pyrogenic water, and then treated with a mixture of 40% glycerol and 60% water, and finally dried with air.

Detailed Description Text - DETX (36):

The membrane thus formed had the three-layer structure hereof, with the inner dense skin layer having a thickness of about 1.mu., the sponge-like substructure having a thickness of about 5.mu. and the outer open finger-like structure having a thickness of about 45.mu..

Detailed Description Text - DETX (38):

Twelve wt. % polyamide was dissolved in 85 wt. % DMSO together with 1% PVP and 2% H.sub.2 O, in the manner described in Example 1. The polymer solution was then cast with a slit jet on a belt, and transported through a precipitation bath containing 68%

water, 2% PVP and 30% DMSO. The flat membrane had a thickness of 60.mu.. After washing, glycerolization and drying the membrane could be wound without support.

Detailed Description Text - DETX (40):

Hollow fiber membranes produced in the manner described in Example 1 were assembled in a dialyzer with a 1.3 m.sup.2 surface area. Ultrafiltration with water was measured therewith to be 250 ml/mm Hg.m.sup.2.h. With whole blood, the ultrafiltration was dependent on flow parameters and blood composition (hematocrite Hct, protein concentration Pct, blood flow and transmembrane pressure), and was influenced by protein concentration polarization. At a blood flow of 300 ml/min a maximum ultrafiltration of 120 ml/min was achieved, with blood of 25% Hct and 65 g/l total protein (see FIG. 7).

Detailed Description Text - DETX (46):

A solution of 13% pA, 3% pVP, 3% H.sub.2 O, and 81% DMSO was spun with a center fluid of 90% H.sub.2 O, 1% PVP and 9% DMSO to form a hollow fiber having the dimensions set forth in Example 1. The hollow fiber had the three-layer integral structure typical for the membranes of the present invention. The sieving coefficient (measured with plasma containing 65 g/l total protein concentration) for .beta..sub.2 -M was measured to be 0.8. In spite of this high sieving coefficient for .beta..sub.2 -M, the sieving coefficient for the total protein was below 0.001.

Claims Text - CLTX (1):

1. A selectively permeable asymmetric membrane suitable for use in hemodialysis comprising a hydrophobic polymer and a hydrophilic polymer, said membrane including a first layer comprising a dense thin skin layer including substantially uniform pore openings defining the selective permeability of said membrane, an intermediate second layer in contact with said first layer in the form of a sponge and having a diffusive permeability higher than that of said first layer, said second intermediate layer supporting said first layer, and a third layer in contact with said second intermediate layer and including a finger-like structure providing mechanical stability for said membrane, said substantially uniform pore openings in said first layer having a size whereby proteins having a molecular weight of at least that of albumin are substantially completely rejected from said membrane.

Claims Text - CLTX (2):

2. The membrane of claim 1 wherein said substantially uniform pore openings in said first layer have a pore size of not greater than about 80 Angstroms.

Claims Text - CLTX (3):

3. The membrane of claim 1 wherein said first layer has a thickness of less than about 1.mu..

Claims Text - CLTX (4):

4. The membrane of claim 1 in the form of a substantially flat sheet.

Claims Text - CLTX (5):

5. The membrane of claim 1 in the form of a hollow fiber, wherein said first layer comprises the inner layer of said hollow fiber and said third layer comprises the outer layer of said hollow fiber membrane.

Claims Text - CLTX (6):

6. The membrane of claim prepared from a polymer mixture including said hydrophobic polymer and said hydrophilic polymer wherein the fraction of said hydrophobic polymer in said mixture is between about 85 and 95% and the fraction of said hydrophilic polymer in said mixture is between about 5 and 15%.

Claims Text - CLTX (7):

7. The membrane of claim 1 wherein said hydrophobic polymer is selected from the group consisting of polyarylsulfone, polycarbonate, polyamide, polyvinylchloride, modified acrylic acid, polyether, polyurethane, polyetherketone, polyacrylonitrile, polypropylene, polyetherimide and copolymers of said polymers.

Claims Text - CLTX (8):

8. The membrane of claim 7 wherein said hydrophobic polymer comprises a polyamide.

Claims Text - CLTX (9):

9. The membrane of claim 1 wherein said hydrophilic polymer is selected from the group consisting of polyvinylpyrrolidone, polyethyleneglycol, polyglycolmonoester, copolymers of polyethyleneglycol with polypropyleneglycol, water soluble cellulosic derivatives, polysorbate, and polyethylene-polypropylene oxide copolymers and mixtures thereof.

Claims Text - CLTX (10):

10. The **membrane** of claim 9 wherein said hydrophilic polymer comprises polyvinylpyrrolidone.

Claims Text - CLTX (11):

11. The **membrane** of claim 1 including an additive selected from the group consisting of non-solvents and relatively weak solvents for said hydrophobic polymer.

Claims Text - CLTX (12):

12. The **membrane** of claim 11 wherein said additive is selected from the group consisting of alcohols, glycerols, **water**, and mixtures thereof.

Claims Text - CLTX (13):

13. The **membrane** of claim wherein said substantially uniform pore openings in said first layer provide said **membrane** with a sieving coefficient for beta-2-microglobulin having a molecular weight of about 11,500 in blood which is at least about 0.6.

Claims Text - CLTX (14):

14. The **membrane** of claim 1 wherein said intermediate second layer has a thickness of between about 1 and 20.mu..

Claims Text - CLTX (15):

15. The **membrane** of claim 14 wherein said intermediate second layer has a thickness of between about 3 and 5.mu..

Claims Text - CLTX (16):

16. The **membrane** of claim 1 wherein said third layer has a thickness of between about 20 and 60.mu..

Claims Text - CLTX (17):

17. The **membrane** of claim 16 wherein said third layer preferably has a thickness of about 40.mu..

Claims Text - CLTX (18):

18. The **membrane** of claim 1 having a logarithmic reduction value of at least about 3 for the rejection of endotoxins.

Claims Text - CLTX (19):

19. A process for manufacturing selectively permeable asymmetric membranes suitable for use in hemodialysis comprising dissolving a hydrophobic polymer in a first solvent so as to prepare a first solution, dissolving a hydrophilic polymer in a second solvent so as to prepare a second solution, mixing said first and second solutions, and introducing said mixture of said first and second solutions into a precipitating liquid so as to form a coagulated membrane therefrom.

Claims Text - CLTX (20):

20. The process of claim 19 including washing said coagulated membrane.

Claims Text - CLTX (21):

21. The process of claim 20 including drying said washed coagulated membrane.

Claims Text - CLTX (29):

29. The process of claim 28 wherein said solvent for said hydrophilic polymer comprises water.

Claims Text - CLTX (34):

34. The process of claim 28 wherein said hydrophobic polymer comprises polyamide, said hydrophilic polymer comprises polyvinylpyrrolidone, wherein said solvent for said hydrophilic polymer comprises water, and said solvent for said hydrophobic polymer comprises dimethylsulfoxide.

Claims Text - CLTX (35):

35. The process of claim 34 wherein said precipitating liquid includes about 70% of said water and about 30% of said dimethylsulfoxide.

Claims Text - CLTX (37):

37. The process of claim 19 including rinsing said coagulated membrane with water, glycerolization of said rinsed membrane, and drying of said membrane.

Claims Text - CLTX (40):

40. The process of claim 39 wherein said additive is selected from the group consisting of alcohol, glycerols, water, and mixtures thereof.

Claims Text - CLTX (41):

41. The **membrane** of claim 1 wherein said substantially uniform pore openings in said first layer have a pore size of between 20 and 200 Angstroms.

Claims Text - CLTX (42):

42. The **membrane** of claim 1 wherein said substantially uniform pore openings in said first layer have a pore size of between 20 and 80 Angstroms.

Current US Original Classification - CCOR (1):

210/500.38

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L5 and diamine and membrane	0

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*DB=JPAB; PLUR=YES; OP=ADJ*L16 L5 and diamine and membrane0 L16*DB=USPT; PLUR=YES; OP=ADJ*L15 L5 and diamine0 L15L14 L11 and diamine1 L14L13 11 and diamine69086 L13L12 L11 and nonanediamine0 L12L11 L10 and therephthalic acid1 L11L10 polyamide and carboxylic acid and membrane4644 L10L9 L4 and film and pore0 L9L8 15 and porous0 L8L7 15 and membrane0 L7L6 3 and membrane219380 L6*DB=JPAB; PLUR=YES; OP=ADJ*L5 L4 and polyamide3 L5

<u>L4</u>	pa6-t	3	<u>L4</u>
<i>DB=DWPI; PLUR=YES; OP=ADJ</i>			
<u>L3</u>	polyamide and carboxylic acid and therepthalic acid	0	<u>L3</u>
<i>DB=JPAB; PLUR=YES; OP=ADJ</i>			
<u>L2</u>	polyamide and carboxylic acid and therepthalic acid	0	<u>L2</u>
<u>L1</u>	polyamide and film and pa6-t	0	<u>L1</u>

END OF SEARCH HISTORY